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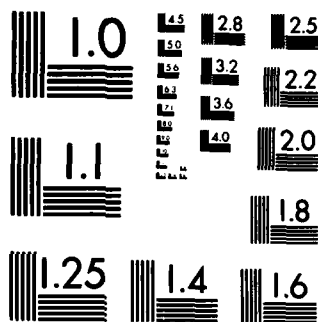
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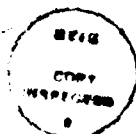
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## 20. Abstract

We have recently completed construction of an energy- and angle-resolved detector for neutral particles desorbed from ion bombarded surfaces. It is based on a time-of-flight measurement for the neutral energies, multiphoton resonance ionization (MPRI) for the angular information. Using this detector, we have initiated a series of experiments aimed at determining the energy and angular distributions of the Rh atoms ejected from clean and adsorbate covered polycrystalline and single crystal surfaces. From the polycrystalline material, we find the velocity distribution of Rh atoms follows closely the form predicted by Thompson with a peak intensity occurring at approximately 5 eV and a high energy tail decreasing in intensity as  $E^{-2}$ . Polar angle distributions exhibit nearly a  $\cos^2$  shape. From a Rh(001) crystal, the velocity distribution generally peaks at a higher value than that found from the polycrystalline surface, and depends strongly on the value of the polar collection angle. In addition to energy distribution measurements into a given angle, we are able to extract angular distribution measurements of particles with a given azimuth from Rh(001) show three peaks of preferred ejection angles. The position of these peaks are predicted well by the classical dynamics calculations.

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FINAL SCIENTIFIC REPORT

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*Secondary Ion Mass Spectrometry Studies of  
Solids and Surfaces*

Grant No. AFOSR-82-0057

*Principal Investigator*

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## I. ABSTRACT

This proposal is aimed toward the development of novel surface analysis methodology through fundamental investigations of secondary ion mass spectrometry and related phenomena. The proposed experiments are based on predictions of a classical dynamics model of the ion bombardment process. Of special interest is to develop suitable theories of ionization of the ejected species which can be incorporated into the classical dynamics model and tested by experiment. These studies will involve both angle-resolved SIMS to examine ion trajectories as well as multi-photon resonance ionization to determine neutral atom trajectories. Furthermore, we will focus on expanding our understanding of the molecular cluster ion process in SIMS. These studies will include the analysis of clusters ejected from a variety of materials including alloys, semi-conductors, organic monolayers on metals as well as a number of well-defined molecular solids. Throughout these investigations we plan to exploit a number of the unique features of SIMS in developing new applications of the technique in the fields of heterogeneous catalysis and electrochemical science.

## II. SUMMARY OF OBJECTIVES AND ACCOMPLISHMENTS

Angular distributions of atoms emitted from ion bombarded single crystals have been known for 20 years to reflect the symmetry of surface atoms.(1-3) These angular anisotropies have also been observed for ions emitted from adsorbate-covered single crystals using angle-resolved SIMS.(4) In the latter case, there are distinct surface channeling mechanisms of the desorbing particle that when coupled to classical dynamics calculations of the ion impact event allow the bonding site of the adsorbed atom or molecule to be determined. Due to the lack of sensitive detectors, no studies have ever been reported on the angular distributions of neutrals desorbed from monolayers. These studies are important for gaining a basic understanding of ion/solid interactions and for making comparisons to trajectories obtained for the secondary ions.

We have recently completed construction of an energy- and angle-resolved detector for neutral particles desorbed from ion bombarded surfaces. It is based on a time-of-flight measurement for the neutral energies, multiphoton resonance ionization (MPRI) for the angular information. The detector is operated in an ultra-high vacuum environment, on well-characterized surfaces, and with low primary ion dosages onto the sample. A schematic representation of the experiment is illustrated in Figure 1. The

desorption is initiated by a  $0.2 \mu\text{s}$ , 5 KeV  $\text{Ar}^+$  ion pulse incident on the sample at  $45^\circ$  focussed to  $0.1 \text{ cm}^2$ , and ionization is accomplished by absorption of photons from a 5 ns laser pulse obtained from the output of a Nd:YAG pumped dye laser. Under the present operating conditions we can detect neutrals whose kinetic energies vary from 0.2-50 eV into a total enclosed angle of over  $100^\circ$ . A complete analysis may be performed using a total dose of less than  $10^{12}$  incident  $\text{Ar}^+$  ions/ $\text{cm}^2$ . A detailed description of the apparatus will be given elsewhere.(5)

Using this detector, we have initiated a series of experiments aimed at determining the energy and angular distributions of Rh atoms ejected from clean and adsorbate covered polycrystalline and single crystal surfaces. Rh atoms may be efficiently and selectively ionized using 312.4 nm laser light, obtained by frequency doubling the output of the dye laser. From the polycrystalline material, we find the velocity distribution of rh atoms follows closely the form predicted by Thompson with a peak intensity occurring at  $\sim 5$  eV and a high energy tail decreasing in intensity as  $E^{-2}$ . Polar angle distributions exhibit nearly a  $\cos^2$  shape. From a Rh{001} crystal, the velocity distribution generally peaks at a higher value than that found from the polycrystalline surface, and depends strongly on the value of the polar collection angle. For example, the energy of the emitted atoms tend to be distributed about higher kinetic energies when the polar angle is chosen to



coincide with a peak in the atom intensities, a result in qualitative agreement with classical dynamics calculations.

In addition to energy distribution measurements into a given angle, we are able to extract angular distribution measurements of particles with a given energy. Polar distribution measurements at a given azimuth from Rh{001} show three peaks of preferred ejection angles. The position of these peaks are predicted well by the classical dynamics calculations. Of particular interest is the peak observed normal to the surface. This normal ejection peak is more prominent at 30 eV than at 10 eV which corresponds to an energy distribution with a larger high-energy tail. Variations in the relative intensity of this center peak relative to the side peaks are observed when an adsorbate such as oxygen or sulfur is placed on the crystal surface. It is hoped that these variations, when coupled to computer simulations of the ion impact event, will lead to a new approach for characterizing such adsorbates.

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13. L. A. DeLouise and N. Winograd, "Carbon Monoxide Adsorption and Desorption on Rh{111} and Rh{331} Surfaces", *Surface Sci.*, 138, 417 (1984).
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15. F. M. Kimock, J. P. Baxter, D. L. Pappas, P. H. Kobrin, and N. Winograd, "Detection of Sputtered Neutrals by Multiphoton Resonance Ionization", 4th International Conference of Secondary Ion Mass Spectrometry, Minoo, Osaka, Japan, Nov. 9-11, 1983, Springer Series in *Chemistry Physics*, 36, 62 (1984).
16. N. Winograd, "Ion Beam Studies of Surfaces by Multiphoton Resonance Ionization of Sputtered Neutrals", Symposium on Atomic and Surface Physics (SASP), Maria Alm, Austria, January 29 - February 4, 1984, page 268.
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20. L. A. DeLouise and N. Winograd, "Reduction of Nitric Oxide on the Carbon Pretreated Rh{331} Single Crystal Surface; Evidence for Molecular CN<sup>-</sup> Formation", *Surface Sci.*, in press.
21. C. Chang, L. A. DeLouise, N. Winograd and B. J. Garrison, "Velocity Dependence of Azimuthal Anisotropies in Ion Scattering from Rhodium{111}", *Surface Sci.*, in press.

22. D. W. Moon, N. Winograd and B. J. Garrison, "Vertical Channeling of Pyridine Molecules Ejected in Ion Bombardment Experiments", *Chem. Phys. Lett.*, in press.
23. L. A. DeLouise and N. Winograd, "Adsorption and Desorption of NO From Rh{111} and Rh{331} Surfaces", *Surface Sci.*, submitted.

#### LECTURES AND TRAVEL RELATED TO GRANT

1. Surface Analysis Symposium, West Chester, PA, "Background and Principles of Surface Analysis", May 25, 1982.
2. Oak Ridge National Laboratory, Oak Ridge, TN, "Ion Beam Spectroscopy of Solids and Surfaces", August 23, 1982.
3. Atom Sciences, Inc., Oak Ridge, TN, "Detection of Sputtered Neutrals by Multi-photon Resonance Ionization", August 24, 1982.
4. 1982 Office of Naval Research Surface Science Meeting, Austin, TX, September 8-9, 1982.
5. Analytical Chemistry Seminar, Ohio State University, Columbus, OH, "Ion Beam Spectroscopy of Surfaces (SIMS)", October 6, 1982.
6. ACS Columbus Section 1982 Fall Lecture Course: Surface Chemistry, Columbus, OH, "Ion Beam Spectroscopy of Surfaces (SIMS)", October 6, 1982.
7. Naval Research Laboratory, Washington, D. C., "Surface Analysis of Ion Beams", December 8, 1982.
8. Arizona Chapter American Vacuum Society Third Annual Symposium, Mesa, AR, "Ion Beam Spectroscopy of Solids and Surfaces", January 31-February 2, 1983.

9. Arizona State University, Tempe, AZ, "Detection of Sputtered Neutrals by Multiphoton Resonance Ionization", February 3, 1983.
10. Chemistry Departmental Colloquium, Rensselaer Polytechnic Institute, Troy, NY, "Ion Beam Spectroscopy of Solids and surfaces", March 3, 1983.
11. Chemistry Departmental Colloquium, University of Colorado, Boulder, CO, "Ion Beam Spectroscopy of Solids and Surfaces", March 28, 1983.
12. Frontiers in Chemistry Lecture, State University of New York, New Paltz, NY, "Use of Secondary Ion Spectrometry (SIMS) in Characterizing Surface Contaminants", April 7, 1983.
13. American Society of Mass Spectrometry, Boston, MA, "Lasers, Mass Spectrometers, and Isotope Ratio Determinations", May 11, 1983.
14. Sixth International Conference on Ion Beam Analysis, Arizona State University, Tempe, AZ, "Detection of Sputtered Neutrals by Multiphoton Resonance Ionization", May 23-27, 1983.
15. Fifth Symposium on Applied Surface Analysis, Dayton, OH, "Laser Ionization of Sputtered Neutrals: A Novel Approach to Materials Characterization", June 8-10, 1983.
16. Semiconductor Research Cooperative Workshop on GaAs, Raleigh, NC, "Surface Structure of MBE Grown Materials", June 12-15, 1983.
17. Sixth International Summer Institute in Surface Science, Milwaukee, WI, "Angle-Resolved SIMS", August 22-26, 1983.
18. Fourth International Conference on Ion Mass Spectrometry, Minoo, Osaka, Japan, "Detection of Sputtered Neutrals by Multiphoton Resonance Ionization", November 13-19, 1983.

19. Symposium on Atomic and Surface Physics, Hintermoos, Austria, "Ion Beam Studies of Surfaces by Multiphoton Resonance Ionization of Sputtered Neutrals", January 29-February 4, 1984.
20. Electronics Institute, Prague, Czechoslovakia, "Ion Beam Studies of Surfaces by Multiphoton Resonance Ionization of Sputtered Neutrals", February 6, 1984.
21. Brookhaven National Laboratory, Long Island, NY, "Ion Beams, Lasers and X-rays! Some Aspects of the Current Renaissance in Surface Science", February 14, 1984.
22. Chemistry Departmental Colloquium, Seton Hall University, Orange, NJ, "Ion Beams, Lasers and X-rays! Some Aspects of the Current Renaissance in Surface Science", February 28, 1984.
23. Chemistry Departmental Colloquium, University of California, Berkeley, CA, "Ion Beams, Lasers and X-rays! Some Aspects of the Current Renaissance in Surface Science", April 3, 1984.
24. Second International Symposium on Resonance Ionization Spectroscopy and Its Applications, Knoxville, TN, "Ion Beam Studies of Surfaces by Multiphoton Resonance Ionization of Sputtered Neutrals", April 16, 1984.
25. Gordon Research Conference on Particle-Solid Interactions, Plymouth, NH, "Emitted Particles and Lasers Excitation", July 13, 1984.
26. National ACS Meeting, Symposium on Photochemical and Electrochemical Surface Science: Techniques for the Characterization of Electrode Surfaces, Philadelphia, PA, "Ion Beam Studies of Metal Surfaces", August 26, 1984.



27. National ACS Meeting, Symposium on Techniques for the Characterization of Electrode Surfaces, Philadelphia, PA, "Ion Beam Studies of Metal Surfaces", August 28, 1984.
28. Amoco Research Center, Naperville, IL, "Ion Beam Studies of Solids and Surfaces", September 25, 1984.
29. Chemistry Departmental Colloquium, University of Cincinnati, Cincinnati, OH, "Ion Beam Spectroscopy of Solids and Surfaces", September 26, 1984
30. Symposium on SIMS and FAB Mass Spectrometry: An Interdisciplinary Discussion, St. Paul, MN, "Angle-Resolved SIMS", October 8, 1984.
31. Optical Society of America, San Diego, CA, "Detection of Sputtered Neutrals by Multiphoton Resonance Ionization", California, October 29, 1984.
32. Greater New York Chapter of the American Vacuum Society, Symposium of Surface Modification by Directed Deposition of Energy, Yorktown Heights, NY, "Multiphoton Ionization of Sputtered Atoms", IBM Laboratories, November 9, 1984.

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